(12) UK Patent Application (19) GB (11) 2 106 938 A

(21) Application No 8129436
(22) Date of filing 29 Sep 1981
(43) Application published
20 Apr 1983
(51) INT CL³
C23C 11/02
(52) Domestic classification
C7F 1B2 2M 4X 5A
U1S 2060 2068 C7F
(56) Documents cited
GB 2057018 A
GB 2051873 A
GB 1470227
GB 1494176
GB 1135016
GB 0984366
(58) Field of search
C7F
B1F
B1T
(71) Applicants
Standard Telephones and Cables Limited,
(Great Britain),
190 Strand,
London WC2R 1DU
(72) Inventors
Erneast James Workman
Stephen John McManus
Eric Langley Bush
Arjumand Bano Akhtar
(74) Agents
M. C. Dennis,
ITT UK Patent Department,
Maidstone Road,
Foots Cray,
Sidcup DA14 5HT

(54) Tantalum coated alumina particles

(57) Processes and apparatus for coating inert particles, e.g. alumina, with tantalum by chemical vapour deposition in a fluidised bed of the particles (3). Tantalum pentachloride is produced immediately prior to introduction thereof into the bed chamber (3) by reacting hydrogen chloride gas with tantalum metal powder in an adjacent reaction chamber (1). The tantalum pentachloride is reduced to tantalum for deposition on the inert particles by hydrogen gas employed as the fluidising medium. Tantalum coated particles in the exhaust gases from the fluidising chamber can be filtered by means of a filtering arrangement (6) including a layer of silicone treated glass cloth (27-Fig. 2) and a layer of alumina paper (26-Fig. 2); the glass cloth surface being scraped periodically by rings (30) to remove accumulated particles. If the substrate particles are very fine, larger particles may be added to assist fluidisation.

Fig.1.

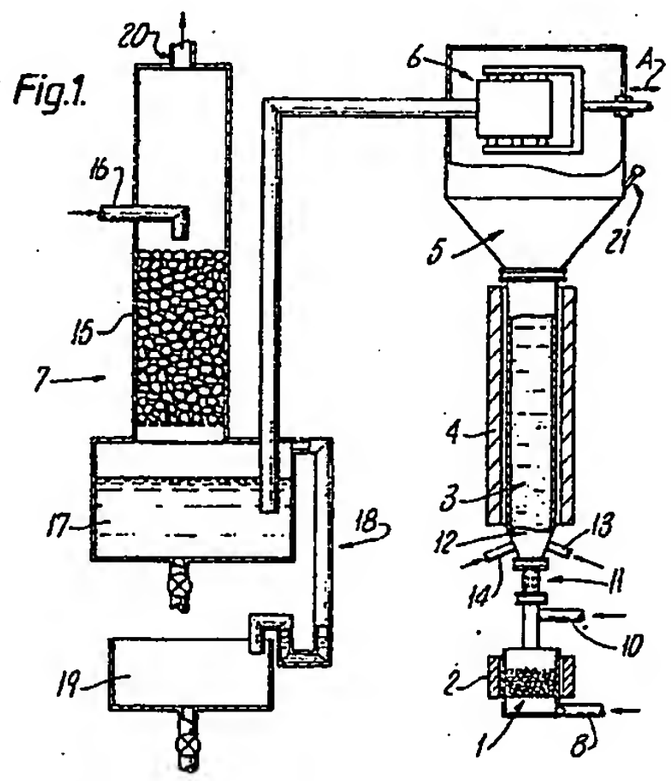
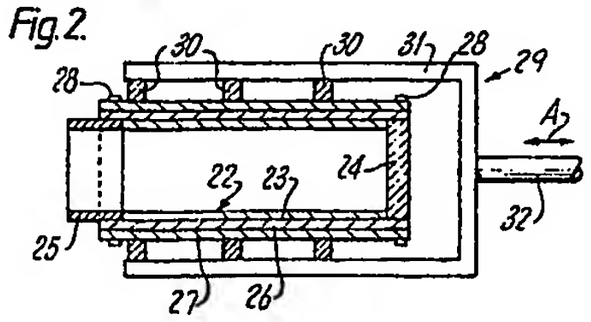


Fig.2.



GB 2 106 938 A

Fig.1.

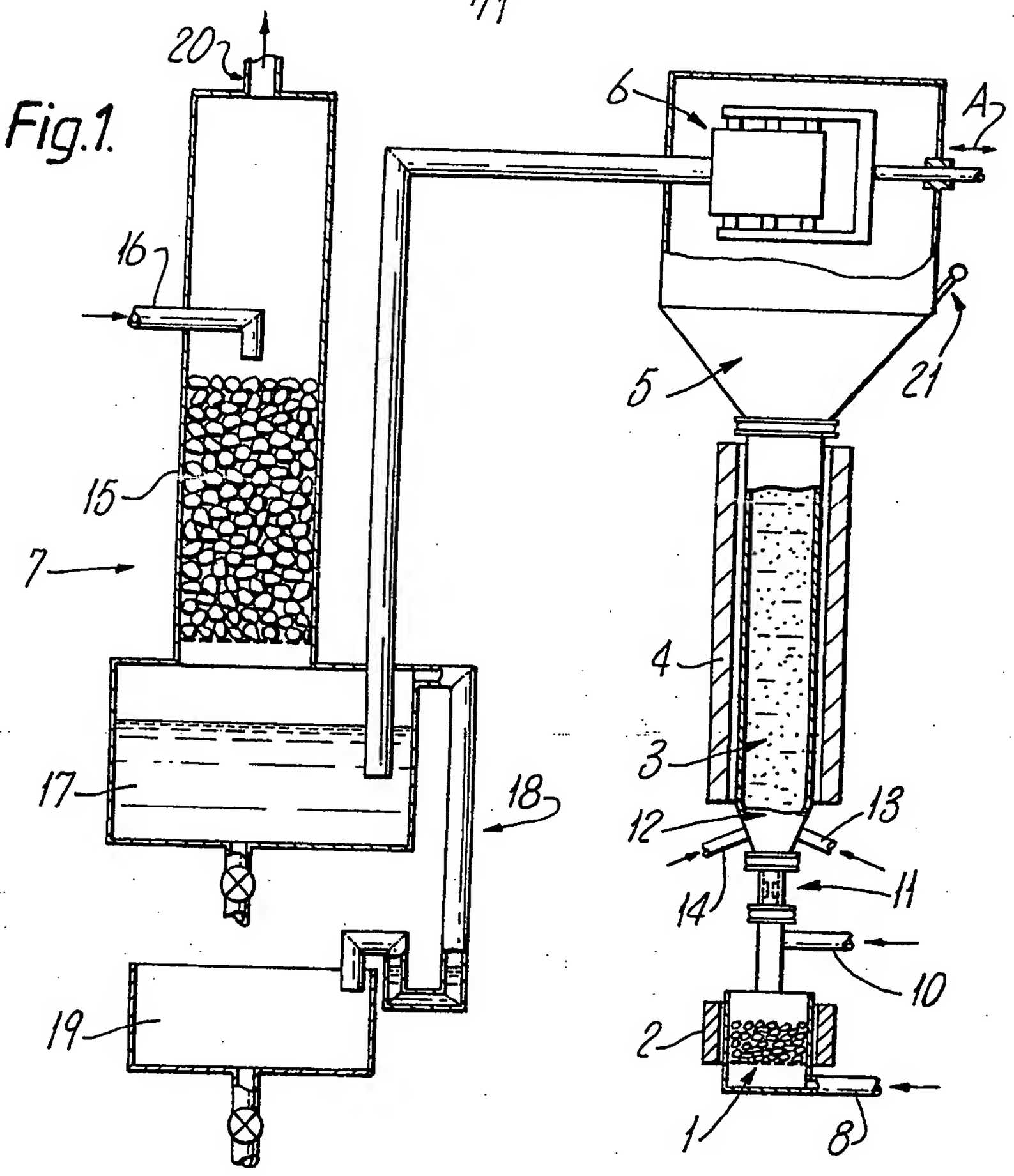
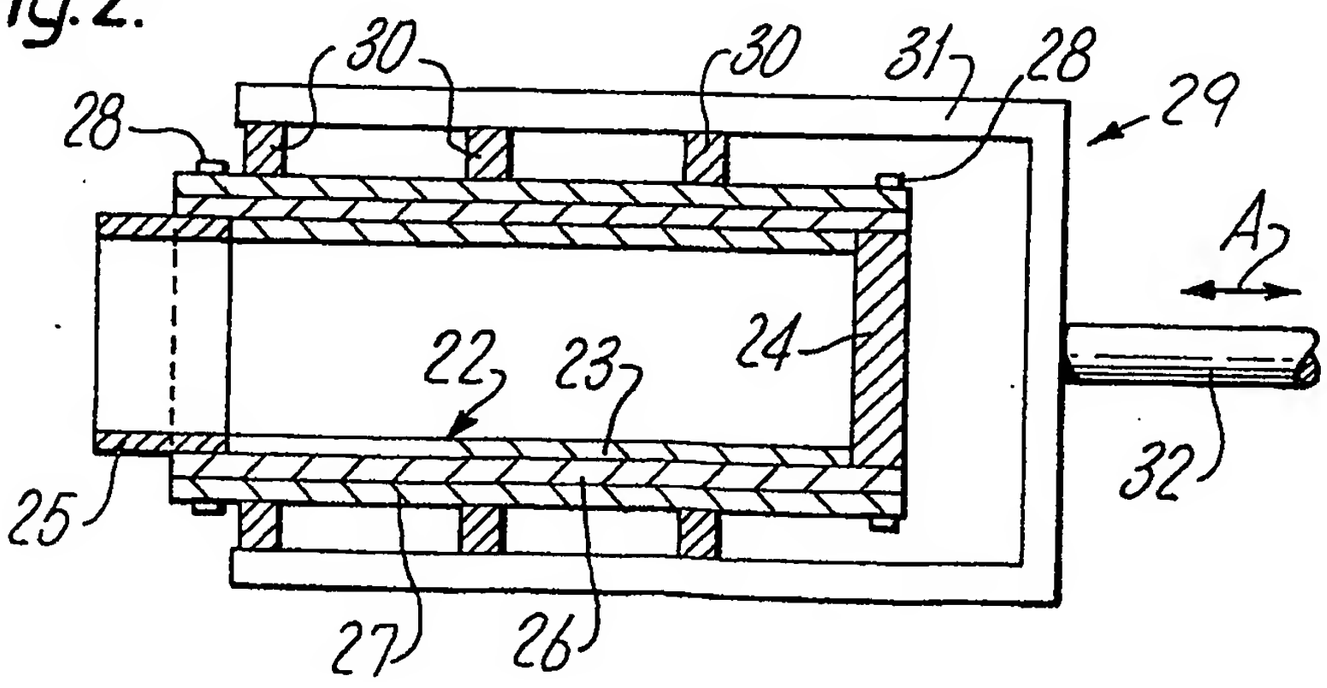


Fig.2.



DOC ID: <GB 2106938A | >

SPECIFICATION

Coating powdered material

This invention relates to processes and apparatus for coating particulate materials, and in particular to chemical vapour deposition of tantalum on inert particles, which coated particles may be compacted to form capacitor anodes of electrolytic capacitors.

Thus for instance particles of an inert material such as alumina may be coated with a layer of tantalum to provide a coated powder which can be compacted to form an anode having similar electrical properties to that of an anode made of particles of comparable size comprised entirely of tantalum. One advantage of using the coated powder is the cost saving resulting from the use of less tantalum. A convenient way of coating the particles is by a chemical vapour reaction process performed in a fluidised powder bed.

According to one aspect of the present invention there is provided a method of coating inert particles with tantalum by chemical vapour deposition in a fluidised bed of the inert particles, the bed being fluidised by hydrogen gas which serves also to reduce tantalum pentachloride, directed into the bed, to tantalum for deposition on the inert particles, and wherein the tantalum pentachloride is produced immediately prior to the direction thereof into the bed by reacting hydrogen chloride gas with tantalum metal powder in a first chamber connected to a second chamber in which the fluidised bed is provided.

According to another aspect of the present invention there is provided a method of coating inert particles with tantalum by chemical vapour deposition in a fluidised bed of the inert particles, the bed being fluidised by hydrogen gas which serves also to reduce tantalum pentachloride, directed into the bed, to tantalum for deposition on the inert particles, including the step of filtering tantalum coated particles from the exhaust gases exiting a chamber in which the fluidised bed is provided by means of a filter including a silicone treated glass cloth layer and an alumina paper layer through which the exhaust gases are passed successively, and including the step of periodically scraping tantalum coated particles from the surface of the silicone treated glass cloth on which the exhaust gases are incident such that the scraped particles fall back towards the fluidised bed.

According to a further aspect of the present invention there is provided apparatus for coating inert particles with tantalum by chemical vapour deposition including a first heatable reaction chamber in which a fluidised bed of the inert particles can be provided in use of the apparatus when a fluidising hydrogen gas stream is passed therethrough from the inlet to the outlet thereof, a second heatable chamber for containing tantalum metal powder through which hydrogen chloride gas is passed in use of the apparatus to provide tantalum pentachloride at the outlet of the second chamber, the outlet of the second chamber being connected to the inlet of the first chamber, means for filtering tantalum coated particles from the exhaust gases exiting from the outlet of the first reaction chamber, and means for scrubbing the filtered exhaust gases to remove unreacted tantalum pentachloride and hydrogen chloride from the hydrogen content thereof.

According to yet another aspect of the present invention there is provided an arrangement for filtering particulate material from a gas including a filter comprised by a cylindrical stainless steel gauze support member, a cylindrical layer comprised of alumina paper arranged on the support member, and a cylindrical layer comprised of silicone treated glass cloth arranged on the alumina paper layer, wherein the gas inlet to the filter is comprised by the radially outermost surface of the glass cloth and the gas outlet of the filter is comprised by the radially innermost surface of the gauze support member, and including scraper means for the periodic removal of accumulated particulate material from the radially outermost surface of the glass cloth.

Embodiments of the present invention will now be described with reference to the accompanying drawings, in which

Fig. 1 shows, somewhat schematically, apparatus for coating particulate materials, and

Fig. 2 shows a cross-section through a filter which can be employed in the apparatus of Fig. 1.

In order to make a coated powder compacted anode that is superior or at least competitive with anodes made of powder consisting exclusively of tantalum, it is generally desirable to use coated powder that has a particle size comparable with that of tantalum powder. In recent years there has been a move towards using finer powders, with resultant fluidisation problems. Our co-pending Application No. 8009410 (Serial No.) (E. L. Bush-E. J. Workman 23-2) discloses methods of overcoming the fluidisation problems associated with fine powders. Basically these methods comprise adding to a fine powder, which is too fine to be readily fluidised, a quantity of a coarser powder that can be fluidised readily, and subsequently sieving out the coarser powder after the tantalum coating process.

The apparatus shown in Fig. 1 basically comprises a reaction chamber 1 and an associated heater 2, a reactor tube (fluidisation chamber) 3 and an associated heater 4, an expansion chamber 5, a filter 6 and a gas scrubbing arrangement 7.

In order to tantalum coat alumina particles, tantalum metal powder is heated to a temperature of between 450 and 550°C in the reaction chamber 1 by heater 2 and hydrogen chloride gas passed into chamber 1 via port 8 and through the metal powder. The tantalum pentachloride which is thus directly formed in the chamber 1 by the reaction

$$2Ta + 10\,HCl \overset{500°C}{\rightleftharpoons} 2TaCl_5 + 5H_2$$

is directed into the reactor tube 3 via duct 9, together with excess hydrogen chloride.

The reactor tube 3 contains a charge comprising a mixture of fine alumina particles and coarse particles in order to facilitate fluidisation as is described in our co-pending Application No. 8009410 mentioned above. The coarse particles may comprise alumina

particles or tantalum coated or partially coated alumina particles, for example, as described in our co-pending Application No. 7918659 (Serial No.) (E. L. Bush-E. J. Workman 21-1) which relates to the introduction of a nucleating agent, such as ammonia, during a valve metal deposition process in order to provide uniform valve metal layers on a particulate insulating substrate.

The charge in the reactor 3 is heated by heater 4 to approximately 1000°C and fluidised by means of hydrogen supplied thereinto via port 10 and a fine jet in assembly 11. The reactor tube 3 includes a cone shaped portion 12 and in order to facilitate charge removal and filling the jet assembly 11 is removably secured to the cone portion 12 and the tube 3 is removably secured to the expansion chamber 5. Initially, as is described in more detail hereinafter, an inert gas such as argon is employed in place of hydrogen. A nucleating gas, such as ammonia, may be introduced as necessary into reactor tube 3 via port 13. Additional hydrogen, for example, may be introduced into the reactor tube 3 via port 14. The tantalum pentachloride is reduced in the reactor tube, by the fluidising hydrogen gas, to metallic tantalum which is uniformally distributed and deposited on the alumina particles. Thus the hydrogen serves for fluidisation and reduction purposes, the reaction for the latter being

$$2TaCl_5 + 5H_2 \xrightarrow{1000°C} 2Ta + 10HCl.$$

Exhaust gas emerging from the top of reaction tube 3 carries powder with it, particularly in view of the high gas velocities used. Expansion chamber 5 serves to reduce the velocity of the gas that flows up from the reactor tube and assist powder removal therefrom. The exhaust gases, which basically comprise hydrogen, hydrogen chloride and unreacted tantalum pentachloride, exit the expansion chamber via filter 6 and are ducted to the scrubbing arrangement 7. Water is passed into a scrubbing tower 15 via inlet 16. The tower contains ceramic dispersion rings. The water flowing through tower 15 is collected in a tank 17 having an overflow 18 and supplementary tank 19. The exhaust gases from filter 6 are passed through the water in tank 17, hydrogen chloride being absorbed by the water. Any hydrogen chloride not collected during passage of the exhaust gases through the absorption tank 17 is removed by the scrubbing tower 15. Hydrogen gas exits the scrubber at port 20 and may be exhausted to the atmosphere, recirculated or otherwise re-employed. Any unreacted tantalum pentachloride is hydrolysed in the absorption tank and converted to tantalum pentoxide. In order to prevent tantalum pentachloride being deposited in the ducting between filter 6 and absorption tank 17 it is advisable to maintain this ducting at approximately 300°C.

The filter 6 serves to prevent tantalum coated powder passing to the scrubbing arrangement 7 and must be appropriately designed in view of the high gas velocities and temperatures involved. The reactor tube temperature is approximately 1000°C, whilst the temperature is lower in the expansion chamber, with the result that tantalum coated powder may collect on the inside walls of the expansion chamber. A rapper or banger illustrated schematically at 21 may be operated periodically to dislodge and therefore minimise the amount of powder collecting on the inside walls of the expansion chamber.

Fig. 2 shows somewhat schematically, and partially in cross-section, a construction of suitable filter 6. A support 22 comprises perforated stainless steel gauze cylinder 23 with a closed end formed by a wall 24 connected thereto and an open end formed by a cylindrical portion 25 connected thereto and for connection to the ducting leading to the scrubbing arrangement. Alumina paper 26 is wrapped around the cylinder 23 and this is in turn wrapped with a silicone treated glass cloth 27. The wrappings are arranged to be as cylindrical as possible and clamped by means of metal wire clamps 28 at each end. In order to remove any build up of coated powder and tantalum pentachloride on the outside wrapping 27 of the filter, which would prevent the exhaust gases from escaping and adversely affect the gas flows and the deposition performance of the reactor, some form of scraper is required to periodically scrape the outside wrapping. The scraper 29 illustrated in Fig. 2 comprises three rings 30 which are a suitable slid fit over the wrapping 27 and which are all mounted to a common structure 31 having an axle member 32. Reciprocation of the axle in the direction of arrow A serves to move the rings 30 over the surface of wrapping 27 and scrape off any powder adhering thereto, which powder subsequently falls back into the reactor tube. The support structure 31 should be such as to provide a minimum impedance to the gas flow to the filter, whilst the rings should be arranged relative to one another so that the whole of the effective surface can be scraped thereby. The rings 30 and associated structure are of a material which will withstand the temperatures involved. The scraper 29 and the rapper 21 may be operated by a common vibrator (not shown).

The basic procedure for operating the apparatus shown in Fig. 1 is as follows. The reaction chamber 1 is filled with tantalum powder and the heaters 2 and 4 employed to raise the temperature of the chamber 1 and tube 3 to approximately 500-600°C whilst argon is passed through both via ports 8 and 10, in order to flush out any oxygen or air which might contaminate the chemical products and create the risk of an explosion with hydrogen.

A suitable charge of, for example, mixed size alumina powder is loaded into the reactor tube 3. The reactor tube is then heated to approximately 800°C and the reaction chamber to approximately 500°C. The argon supply through port 10 is replaced by hydrogen at, for example, a flow rate of 25 litres per minute for a 2 metre long, 10 cm internal diameter, reactor tube which is typically made of Inconel. The argon flow is maintained through the reaction chamber 1. The reactor tube is heated to approximately 1000°C. With a well fluidised bed the temperature of the cone portion, which is indicative of the degree of fluidisation, should be not less than 350°C. The argon flow through the reaction chamber 1 is replaced by hydrogen chloride gas at a predeter-

mined flow rate, typically 2 to 4 litres per minute. The hydrogen chloride gas reacts with the heated tantalum powder to produce tantalum pentachloride. The nucleating gas is introduced through port 13 as necessary. Typically at the start of tantalum deposition on the alumina powder ammonia may be introduced for one hour at a flow rate twice that of the hydrogen chloride gas and then turned off and the hydrogen chloride gas flow adjusted as necessary for a required deposition rate. Deposition is carried out for the time appropriate to the required tantalum thickness, typically 12 hours to obtain a coated powder containing approximately 55% by weight of tantalum on a charge containing 3.5 kg of 3μ alumina powder and 1.5 kg of 120μ partially tantalum coated alumina powder.

At the end of the deposition time the reaction chamber 1 is allowed to cool to about 200°C with argon passing therethrough whilst the reactor tube is allowed to cool to about 800°C with hydrogen passing therethrough. Then the whole apparatus is allowed to cool with argon passing therethrough to a suitable temperature for unloading the charge.

Whilst the invention has been described with reference to mixed size alumina particles in order to achieve acceptable fluidisation, for "larger" particles than the "finer" particles generally employed at present it may be unnecessary to add large particles to achieve acceptable fluidisation.

The filter and scraping means may alternatively be employed with a fluidised bed reactor to which tantalum pentachloride is supplied in a conventional way, rather than the in tandem production method described above.

Tantalum pentachloride is a solid at normal temperatures but becomes liquid at approximately 200°C. It is very corrosive and thus difficult to handle. The basic advantage of the in situ production of tantalum pentachloride as described above is that the production thereof is controlled simply by the switching on or off of a tap at room temperature controlling the admission of hydrogen chloride gas to the tantalum containing reaction chamber. This also facilitating handling of the tantalum pentachloride.

CLAIMS

1. A method of coating inert particles with tantalum by chemical vapour deposition in a fluidised bed of the inert particles, the bed being fluidised by hydrogen gas which serves also to reduce tantalum pentachloride, directed into the bed, to tantalum for deposition on the inert particles, and wherein the tantalum pentachloride is produced immediately prior to the direction thereof into the bed by reacting hydrogen chloride gas with tantalum metal powder in a first chamber connected to a second chamber in which the fluidised bed is provided.

2. A method as claimed in claim 1, wherein the tantalum metal powder is heated in the first chamber to a temperature in the range 450 to 550°C.

3. A method as claimed in claim 1 or claim 2, wherein the reduction is carried out at a second chamber temperature of approximately 1000°C.

4. A method as claimed in any one of the preceding claims, wherein the inert particles to be coated are too fine to be readily fluidised on their own, and wherein the inert particles are admixed with a sufficient quantity of an additional coarse powder of a substantially larger particle size, large enough to be capable of being fluidised on its own in the second chamber.

5. A method as claimed in any one of the preceding claims including introducing a nucleating agent into the first chamber during tantalum deposition.

6. A method as claimed in any one of the preceding claims including the step of filtering tantalum coated particles from the exhaust gases exiting the second chamber by passing it through silicone treated glass cloth and subsequently passing it through alumina paper.

7. A method as claimed in claim 6, including the step of periodically scraping the surface of the silicone treated glass cloth on which the exhaust gases are incident.

8. A method as claimed in any one of the preceding claims wherein adjacent the second chamber an expansion chamber is provided through which the exhaust gases pass, and including the step of periodically rapping the expansion chamber wall to dislodge tantalum coated particles collecting thereon.

9. A method of coating inert particles with tantalum by chemical vapour deposition in a fluidised bed of the inert particles, the bed being fluidised by hydrogen gas which serves also to reduce tantalum pentachloride, directed into the bed, to tantalum for deposition on the inert particles, including the step of filtering tantalum coated particles from the exhaust gases exiting a chamber in which the fluidised bed is provided by means of a filter including a silicone treated glass cloth layer and an alumina paper layer through which the exhaust gases are passed successively, and including the step of periodically scraping tantalum coated particles from the surface of the silicone treated glass cloth on which the exhaust gases are incident such that the scraped particles fall back towards the fluidised bed.

10. A method of coating inert particles with tantalum substantially as herein described with reference to Fig. 1, or Figs. 1 and 2, of the accompanying drawings.

11. Apparatus for coating inert particles with tantalum by chemical vapour deposition including a first heatable reaction chamber in which a fluidised bed of the inert particles can be provided in use of the apparatus when a fluidising hydrogen gas stream is passed therethrough from the inlet to the outlet thereof, a second heatable chamber for containing tantalum metal powder through which hydrogen chloride gas is passed in use of the apparatus to provide tantalum pentachloride at the outlet of the second chamber, the outlet of the second chamber being connected to the inlet of the first chamber, means for filtering tantalum coated particles from the exhaust gases exiting from the outlet of the first reaction chamber, and means for scrubbing the filtered exhaust gases to remove unreacted tantalum pentachloride and hydrogen chloride from the hydrogen content thereof.

12. Apparatus as claimed in claim 11 wherein the filtering means is arranged in an expansion chamber arranged at the outlet of the first reaction chamber.

13. Apparatus as claimed in claim 11 or claim 12, wherein the filtering means includes a silicone treated glass cloth layer and an alumina paper layer through which the exhaust gases are passed successively and means for periodically scraping tantalum coated particles from the surface of the silicone treated glass cloth on which the exhaust gases are incident.

14. Apparatus as claimed in claim 13, wherein the filtering means includes a cylindrical stainless steel gauze support member, the alumina paper layer comprising a cylindrical layer on the support member and the silicone treated glass cloth comprising a cylindrical layer on the alumina paper cylindrical layer.

15. Apparatus as claimed in claim 14, wherein the scraping means include one or more rings engageable for scraping with the outermost surface of the silicone treated glass cloth and reciprocable relative to the axis of the cylinder whereby to scrape tantalum coated particles from the entire outermost surface of the silicone treated glass cloth which is effective for filtering purposes.

16. An arrangement for filtering particulate material from a gas including a filter comprised by a cylindrical stainless steel gauze support member, a cylindrical layer comprised of alumina paper arranged on the support member, and a cylindrical layer comprised of silicone treated glass cloth arranged on the alumina paper layer, wherein the gas inlet to the filter is comprised by the radially outermost surface of the glass cloth and the gas outlet of the filter is comprised by the radially innermost surface of the gauze support member, and including scraper means for the periodic removal of accumulated particulate material from the radially outermost surface of the glass cloth.

17. Apparatus for coating inert particles with tantalum by chemical vapour deposition, substantially as herein described with reference to and as illustrated in Fig. 1, or Figs. 1 and 2, of the accompanying drawings.

18. An arrangement for filtering particulate material from a gas substantially as herein described with reference to and as illustrated in Fig. 2 of the accompanying drawings.

19. A method of coating inert particles with tantalum by chemical vapour deposition in a fluidised bed of the inert particles, the bed being fluidised with hydrogen gas which serves also to reduce tantalum pentachloride, directed into the bed, to tantalum for deposition on the inert particles, including the steps of filtering tantalum coated particles from the exhaust gases exiting a chamber in which the fluidised bed is provided by means of a filter and scraping accumulated particulate from the filter.

New claims or amendments to claims filed on 27 November 1981.

Superseded claims 5, 8, 11, 12.

5. A method as claimed in any one of the preceding claims including introducing a nucleating agent into the second chamber during tantalum deposition.

8. A method as claimed in any one of the preceding claims wherein the second chamber includes an expansion chamber portion through which the exhaust gases pass, and including the step of periodically rapping the expansion chamber wall to dislodge tantalum coated particles collecting thereon.

11. Apparatus for coating inert particles with tantalum by chemical vapour deposition including a first heatable reaction chamber, a second heatable reaction chamber in which a fluidised bed of the inert particles can be provided in use of the apparatus when a fluidising hydrogen gas stream is passed therethrough from the inlet to the outlet thereof, the first heatable chamber being for containing tantalum metal powder through which hydrogen chloride gas is passed in use of the apparatus to provide tantalum pentachloride at the outlet of the first chamber, the outlet of the first chamber being connected to the inlet of the second chamber, means for filtering tantalum coated particles from the exhaust gases exiting from the outlet of the second reaction chamber, and means for scrubbing the filtered exhaust gases to remove unreacted tantalum pentachloride and hydrogen chloride from the hydrogen content thereof.

12. Apparatus as claimed in claim 11 wherein the filtering means is arranged in an expansion chamber portion of the second reaction chamber.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1983.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.